Espresso Coffee

The Science of Quality

Second edition

Edited by

ANDREA ILLY
and
RINANTONIO VIANI

with the assistance of Furio Suggi Liverani

ELSEVIER
ACADEMIC
PRESS

AMSTERDAM BOSTON HEIDELBERG LONDON NEW YORK OXFORD
PARIS SAN DIEGO SAN FRANCISCO SINGAPORE SYDNEY TOKYO

IPR2023-00485
Nespresso USA, Inc. Ex. 1056
Page 1 of 34

This book is printed on acid-free paper

First published 1995
Second edition 2005

Copyright © 1995, 2005, Illycaffè s.p.a. All rights reserved.

No part of this publication may be reproduced, stored in a retrieval system, or transmitted in any form or by any means electronic, mechanical, photocopying, recording or otherwise, without the prior written permission of the publisher

Permissions may be sought directly from Elsevier's Science & Technology Rights Department in Oxford, UK: phone: (+44) 1865 843830, fax: (+44) 1865 853333, e-mail: permissions@elsevier.co.uk. You may also complete your request on-line via the Elsevier homepage (http://www.elsevier.com), by selecting 'Customer Support' and then 'Obtaining Permissions'

Elsevier Academic Press
525 B Street, Suite 1900, San Diego, California 92101-4495, USA
http://www.elsevier.com

Elsevier Academic Press
84 Theobald's Road, London WC1X 8RR, UK
http://www.elsevier.com

British Library Cataloguing in Publication Data
A catalogue record for this book is available from the British Library

Library of Congress Catalog Number: 2004113615

ISBN 0-12-370371-9

Printed and bound in Italy
05 06 07 08 09 9 8 7 6 5 4 3 2 1

Working together to grow
libraries in developing countries
www.elsevier.com | www.bookaid.com | www.sabre.com
ELSEVIER BOOK AID International Sabre Foundation

Contents

Contributors ix
Acknowledgements xvii

1 Quality **1**
A. Illy
1.1 Origins and meanings of quality 1
1.2 Definition of quality 2
1.3 Commercial quality 3
1.4 Quality of food products 7
1.5 The experience of coffee consumption 10
1.6 The quality of espresso coffee 15
1.7 Definition of espresso 16
1.8 Conclusions 19
References 20

2 The plant **21**
F. Anzueto, T.W. Baumann, G. Graziosi, C.R. Piccin, M.R. Söndahl and H.A.M. van der Vossen
2.1 Origin, production and botany 21
2.2 Variety development 29
2.3 Agronomy 34
2.4 Biochemical ecology 55
2.5 Molecular genetics of coffee 67
References 76

3 The raw bean **87**
S. Bee, C.H.J. Brando, G. Brumen, N. Carvalhaes, I. Kölling-Speer, K. Speer, F. Suggi Liverani, A.A. Teixeira, R. Teixeira, R.A. Thomaziello, R. Viani and *O.G. Vitzthum*
3.1 Introduction 87
3.2 Harvesting 87
3.3 Processing of the harvest 91
3.4 Drying 96

IPR2023-00485
Nespresso USA, Inc. Ex. 1056
Page 3 of 34

3.5 Final processing for export and roasting 101
3.6 Logistics 108
3.7 Defects 116
3.8 Classification: physical and sensorial analysis 134
3.9 Blending 141
3.10 Decaffeination 142
3.11 Raw bean composition 148
References and further reading 166

4 Roasting 179
B. Bonnländer, R. Eggers, U.H. Engelhardt and H.G. Maier
4.1 The process 179
4.2 Roasting techniques 184
4.3 Changes produced by roasting 191
4.4 Volatile aroma compounds 197
4.5 Melanoidins 204
4.6 Contaminants 209
References 209

5 Grinding 215
M. Petracco
5.1 Theory of fracture mechanics 216
5.2 Coffee grinders 218
5.3 Methods for measuring ground product fineness 221
5.4 Parameters influencing grinding 224
5.5 Physico-chemical modifications due to grinding 227
References 229

6 Storage and packaging 230
M.C. Nicoli and O. Savonitti
6.1 Physical and chemical changes of roasted coffee during storage 230
6.2 Packaging of roasted coffee 245
References 255

7 Percolation 259
M. Petracco
7.1 Conceptual definitions 259
7.2 Physical and chemical characterization of the percolation process 261
7.3 Modelling of the percolation process 266
7.4 The espresso machine 270

IPR2023-00485
Nespresso USA, Inc. Ex. 1056
Page 4 of 34

7.5 Parameters influencing percolation 274
References 287

8 The cup 290
M. Petracco
8.1 Physical and chemical characterization of the espresso beverage 290
8.2 Organoleptic characteristics of espresso (practical aspects) 300
8.3 Espresso definition again 310
8.4 Espresso–milk mixes 311
References 313

9 Physiology of perception 316
R. Cappuccio
9.1 Introduction 316
9.2 Gustation 317
9.3 Olfaction 325
9.4 Human chemosensory psychophysics 332
References 345

10 Coffee consumption and health 352
M. Petracco and R. Viani
10.1 Consumption patterns 353
10.2 Coffee is more than caffeine 357
10.3 Coffee is beneficial to health 357
10.4 Coffee is not harmful to health 365
10.5 Conclusions 369
References 369

Closing remarks 384
E. Illy

Index 385

CHAPTER 6

Storage and packaging

M.C. Nicoli and O. Savonitti

6.1 PHYSICAL AND CHEMICAL CHANGES OF ROASTED COFFEE DURING STORAGE

M.C. Nicoli

Roasted coffee is a shelf-stable product. In fact, thanks to the high temperatures attained in the roasting process and to its low water activity (a_w), no enzymatic and microbial spoilage occurs. However, during storage, coffee undergoes important chemical and physical changes, which greatly affect quality and acceptability of the brew. These events are responsible for staling of roasted coffee but they are also believed to be involved in the so-called ageing process. The border existing between ageing and staling is unclear, and the reactions which prevail in ageing with respect to staling are still unknown. Ageing is a short length of time, just after roasting, in which coffee is allowed to rest under proper technological conditions for improving its sensorial properties. Although many of the physical and chemical changes occurring in roasted coffee during storage are considered unavoidable, the rate at which they occur mostly depends on some environmental and processing variables such as oxygen and moisture availability, exposed surface as well as packaging conditions. The adoption of proper grinding and packaging conditions can greatly slow down staling reactions. However, they can be accelerated again, proceeding at a considerable rate, after the consumer opens the packaging. In fact, home storage conditions, mainly in terms of oxygen availability, relative humidity and temperature, are the key factors in determining the so-called secondary shelf life of the product (Full *et al.*, 2001).

Table 6.1 summarizes the most important physical and chemical events that take place in roasted coffee during storage.

Solubilization and adsorption represent the main mechanisms through which aroma compounds are retained into the bean structure. In fact,

IPR2023-00485
Nespresso USA, Inc. Ex. 1056
Page 6 of 34

Table 6.1 Physical and chemical changes occurring in roasted coffee during storage

Volatile solubilization	CO_2 release
Volatile adsorption	Oxidations
Volatile release	Oil migration

volatiles, as well as carbon dioxide, can exist entrapped in the pores, dissolved in coffee oils and moisture and probably adsorbed into active sites (Labuza *et al.*, 2001). This represents an important requisite for obtaining a high quality coffee cup. However, volatile compounds are easily released in the vapour phase due to diffusion mechanisms. The latter, together with oxidation reactions, are considered the main causes of coffee staling. The evolution of carbon dioxide, which is the most important non-aromatic volatile found in fresh roasted coffee, represents an additional problem during storage, mainly from a technological point of view. In fact, in the case of use of flexible pouches, it causes a rapid loss in the package integrity due to swelling and bursting. The amount of CO_2 formed depends on the degree of roasting and can be up to 10 ml/g (SPT), corresponding to 1–2% of roasted coffee weight (Sivetz and Desrosier, 1979). For this reason, different procedures such as degassing or pressurization, together with the adoption of suitable packaging solutions, have been developed in order to allow carbon dioxide to be released, minimizing aroma losses and oxidations (see 6.2).

Since roasted coffee is a dehydrated product, the major factors controlling its stability during storage are oxygen concentration (O_2), water activity (a_w) – particularly if roasting had been quenched by adding water – and temperature. Technological operations such as grinding, degassing and packaging may accelerate the above-mentioned changes due to the increase in the exposed surface, as well as in oxygen and moisture availability. In addition, since the pressure in the bean pores should be greater than atmospheric pressure, the external pressure applied to the coffee beans represents an additional variable to be considered for enhancing coffee stability during storage. In fact, as the external pressure becomes higher than the partial pressure of volatiles present in the beans, the degassing rate is reduced allowing a larger quantity of volatiles to be dissolved in the lipid fraction or adsorbed on the active sites (Clarke, 1987a; Labuza *et al.*, 2001).

IPR2023-00485
Nespresso USA, Inc. Ex. 1056
Page 7 of 34

6.1.1 The role of Maillard reaction products on roasted coffee stability during storage (see also 4.5)

Coffee staling takes its origin from roasting. Maillard reaction and pyrolysis, which are the main chemical events occurring in coffee during roasting, transform the beans into a very unstable and reactive system. In broad terms, the most macroscopic changes occurring in coffee during roasting and storage can be attributed to the formation of Maillard reaction products (MRPs) and carbon dioxide. The latter is a reaction product from both Maillard reaction and pyrolysis (Hodge, 1953; Yaylayan and Huyghues-Despointes, 1994). The formation of volatiles and CO_2 during roasting causes the expansion of the beans due to the internal build-up of gases which, along with the high temperatures, allows internal pores and pockets to be formed. However, the increased CO_2 formation in the advanced stages of the roasting process corresponds to a progressive reduction of the ability of the bean to entrap and retain CO_2 and other volatiles, as the bean loses its elasticity and surface cracks are formed under the push of the increased internal pressure (Massini *et al.*, 1990). A comparison between the amount of CO_2 formed during roasting and retained into the bean during storage is shown in Figure 6.1.

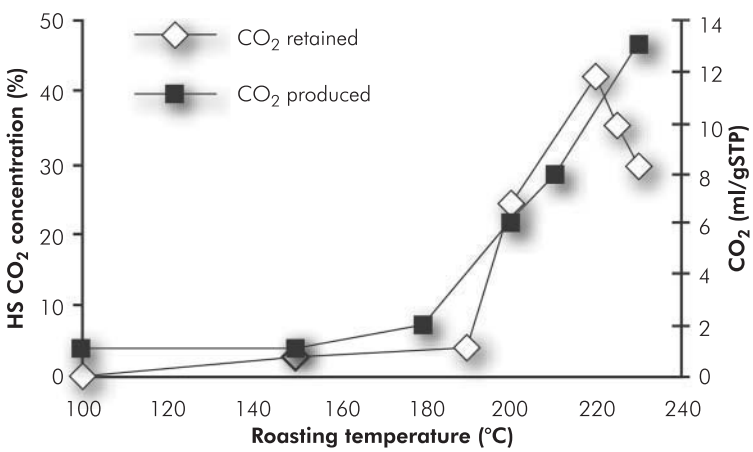

Figure 6.1 Comparison between amount of CO_2 produced during roasting and retained into the coffee beans (data elaborated from Barbera, 1967; Massini *et al.*, 1990). Values of CO_2 retained are referred to the percentage of CO_2 present in the headspace in equilibrium with the sample after 5 minutes' storage after roasting

IPR2023-00485
Nespresso USA, Inc. Ex. 1056
Page 8 of 34

It can be observed that, as the bean temperature rises during roasting, increased amounts of CO_2 are formed. However, this corresponds to a progressive loss of the CO_2 retention capacity of the bean. Among the hundreds of compounds generally considered as MRPs, volatiles and melanoidins play a key role in determining the aroma and body of the coffee brew. Also, the development of the Maillard reaction during roasting is responsible for other important changes affecting coffee stability during storage. The most important effects exerted by MRPs in roasted coffee are summarized in Table 6.2.

Many of the low molecular weight MRPs are responsible for the formation of the typical coffee flavour. It is well known that the aroma profile of roasted coffee is given by several hundreds of compounds covering many different chemical classes. The development of the typical stale flavour of old coffee is the sum of two different actions: the partition of volatiles in the vapour phase and the development of off-flavours as the result of their oxidation. It has been observed that methanethiol, Strecker aldehydes and α-dicarbonyls are the most important low-boiling compounds responsible for the freshness of coffee aroma (Steinhardt and Holscher, 1991). These molecules, in addition to their high volatility, are particularly prone to oxidation. However, it must be pointed out that the aroma perception could also be affected by the ability of melanoidins to bind specific volatile molecules, as recently observed for some thiol compounds by Hofmann *et al.* (2001).

Most of the effects of MRPs on the shelf life of roasted coffee trace their origin to the ability of these compounds to act as both pro-oxidants and antioxidants. These contradictory functions may be explained by the complex and different chemical structures of MRPs. In broad terms, while melanoidins are generally recognized to be strong antioxidants, uncoloured compounds, such as those formed during the early and intermediate stages of Maillard reaction, may exert pro-oxidant activity, being

Table 6.2 Significance of MRPs in coffee during storage

Flavour	Shelf life
Volatile formation	Oxidation reactions: Degradation of aroma compounds Lipid oxidation slow-down Microbial growth inhibition
Volatile binding	

IPR2023-00485
Nespresso USA, Inc. Ex. 1056
Page 9 of 34

in most cases radicals (Namiki, 1990; Manzocco *et al.*, 2001, 2002). During storage, radical reactions may occur leading to the formation of non-radical forms as well as to the generation of radical species chemically different from those initially present (Goodman *et al.*, 2001).

Among melanoidins, recent findings suggest that the fraction of low molecular weight melanoidins (MW<1000–3000 Da) shows higher antioxidant efficiency than that of high molecular weight (MW up to 150 000) (Hofmann, 2000). These compounds seem to act both as primary and as secondary antioxidants since they have been found to behave as chain-breakers, reducing compounds and metal chelators (Homma *et al.*, 1986; Nicoli *et al.*, 1997). The antioxidant capacity of roasted coffee can greatly vary depending on the roasting degree. In Table 6.3 data of chain-breaking activity and redox potential with reference to light, medium and dark coffee samples are reported.

While the assessment of the chain-breaking activity allows estimation of the quenching rate of coffee compounds towards reference radicals, the redox potential gives indications on the effective oxidation/reduction efficiency of all the antioxidants present, including the 'slow' ones, which cannot be detected by the traditional chain-breaking kinetic assays. 'Slow' antioxidants are expected to play an important role in determining the shelf life of roasted coffee during storage (Nicoli *et al.*, 2004). While slight changes in the chain-breaking activity can be observed from light to dark roasted coffees, indicating the existence of a balance between the anti-radical efficiency of naturally occurring antioxidants, which are degraded during roasting, and the heat-induced ones, the redox potential significantly decreases. This indicates that MRPs show higher reducing properties than natural antioxidants. In broad terms, this means that dark

Table 6.3 Chain-breaking activity and redox potential values of coffee samples having different roasting degree

Sample	Weight loss (%)	Chain-breaking activity ($-Abs^{-3}\ min^{-1} mg_{ss}^{-1}$)	Redox potential (mV)
Raw	0	0.320±0.13*	109
Light	14.5	0.273±0.03*	45
Medium	16.2	0.283±0.13*	−2
Dark	18.9	0.390±0.04	−35

*Data not significantly different.
The chain-breaking activity assay was performed using the DPPH test (Nicoli *et al.*, 2001).

IPR2023-00485
Nespresso USA, Inc. Ex. 1056
Page 10 of 34

roasted coffee is expected to have a greater antioxidant reservoir potentially available during storage.

The presence of such reactive species in roasted coffee can explain the huge variety of redox and radical reactions occurring in coffee during storage and even, at an increased rate, after beverage extraction (Nicoli *et al.*, 2001; Anese and Nicoli, 2003). The oxidation of these reactive compounds has a double relation with roasted coffee shelf life: they are the main cause of aroma compounds degradation, but they also represent an efficient barrier against the oxidation of the lipid fraction. In fact, despite the very low a_w value, lipids in coffee show an extraordinary stability against oxidation thanks to the presence of lipid-soluble MR antioxidants (Whitfield, 1992). Figure 6.2 shows the influence of melanoidins on the stability of coffee lipids. It is interesting to note that samples previously freed from melanoidins showed lower oxidation stability as compared to that measured for lipids containing melanoidins. The antioxidant efficiency of melanoidins has been found to be strictly related to the intensity of the heat treatment used to allow their formation. The higher the intensity of heating, the higher their intrinsic antioxidant capacity (Anese *et al.*, 2000). For dark roasted coffee, the stability of the lipid fraction was observed to range from 4 to 10 months at 25 °C storage depending on oxygen availability and packaging conditions (Nicoli *et al.*, 1993).

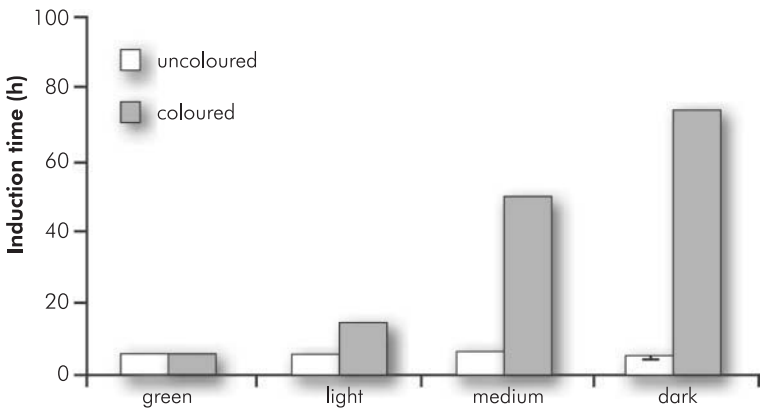

Figure 6.2 Influence of lipid-soluble melanoidins on oxidation stability of coffee lipids (from Anese *et al.*, 2000). The uncoloured samples were obtained by removing melanoidins with active carbon. Data are expressed as induction time (hours) prior to oxidation detected by Rancimat test

IPR2023-00485
Nespresso USA, Inc. Ex. 1056
Page 11 of 34

The ability of MRPs to act as antioxidants can in part explain their inhibiting action against the growth of some food-poisoning microorganisms. However, the extent of MRPs antimicrobial activity appears to be linked to their concentration and to the bacteria tested, indicating that different mechanisms other than radical scavenging activity may be involved, since diluted coffee shows a weaker antibacterial activity than concentrated coffees. In addition, the extent of the antimicrobial activity strictly depends on the species tested (Einarson, 1987; Sheikh-Zeinoddin *et al.*, 2000; Daglia *et al.*, 2000).

An increasing interest towards coffee MRPs is justified by the fact that, by virtue of their antioxidant activity, they are expected to exert a range of positive health effects on the human organism (O'Brian and Morissey, 1989; Faist and Erbesdobler, 1999). Thus, the preservation of the intrinsic antioxidant properties of roasted coffee during storage could be of a certain importance to obtain coffee products with high functional properties. Unfortunately, up to now no data are available about the influence of different environmental and processing conditions on the evolution of the overall antioxidant properties of roasted coffee during storage.

6.1.2 Staling kinetics

6.1.2.1 Degassing

Carbon dioxide formed during roasting is trapped in the cellular structure of the bean and is only released over a period of weeks following roasting, resulting in a 1.5–1.7% weight loss. The amount of gas released can be estimated at 6–10 litres per kilogram of beans depending on roasting degree, the higher figures being valid for dark roasted blends (Clarke, 1987b), recently confirmed by the results of Shimoni and Labuza (2000).

Degassing rate is inversely related to time from roasting. The massive degassing that takes place in the early hours after roasting slows down gradually, and it may take months for all the CO_2 to be released from the beans. The process is slow because much of the CO_2 is bound to the bean structure. From a physico-chemical point of view, carbon dioxide in the coffee bean can be solubilized partly in the lipid phase, partly in the water (moisture). Some will be adsorbed on the apolar sites, and, finally, a part will be blocked within the pores, which have collapsed because of the phase changes in the structure of the bean due to the roasting process.

The amount of CO_2 adsorbed in the lipid and aqueous fractions can be roughly estimated at 15×10^{-5} mg of CO_2 per gram of fresh roasted coffee in the lipid phase, and 2.13×10^{-5} mg of CO_2 per g of fresh roasted

IPR2023-00485
Nespresso USA, Inc. Ex. 1056
Page 12 of 34

and ground coffee in water, considering coffee in air at normal CO_2 pressure (Shimoni and Labuza, 2000; Labuza *et al.*, 2001).

The driving force at the basis of carbon dioxide and volatile release from roasted coffee is given by a diffusion flow due both to concentration and pressure gradients. The release begins at a considerable rate just after the end of roasting; then it gradually slows down as the CO_2 and volatile concentration in the headspace increases, reducing the mass transfer driving force.

Figure 6.3 shows an example of CO_2 and volatiles released from roasted coffee beans and roasted ground coffee.

Recent studies carried out by Labuza *et al.* (2001) suggest that CO_2 release from ground coffee is controlled by two different mechanisms: at the beginning the diffusion is regulated by pressure gradients between the outside and the inside of the coffee particles, then by molecular diffusion. The time at which the changeover in mechanism occurs in STP is about 120 min. The few data available about volatile partition kinetics from roasted coffee packed in air indicate that the rates of CO_2 and volatiles release are of the same magnitude. The volatiles present in the headspace at equilibrium with the product after three days' storage were 50%, 35% and 18% at 4, 24 and 40 °C respectively. As regards CO_2 evolution, the residual gas percentage in the headspace after the same storage time and temperature was 63%, 37% and 18% (Nicoli *et al.*, 1993).

As mentioned above, the rate of volatile compounds and gas release from coffee is strongly affected by temperature. Additional factors are pressure, particle size distribution, and during the degassing process, packing, bed depth and entrainment gas composition.

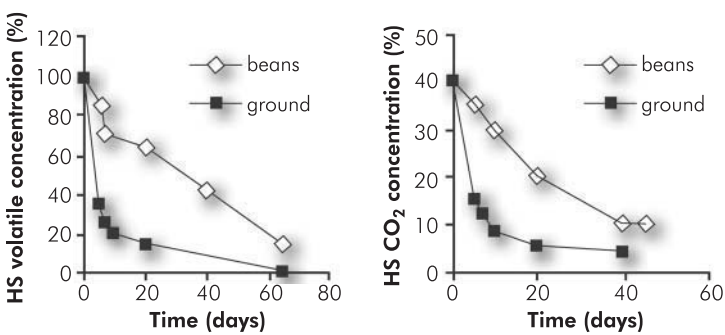

Figure 6.3 Changes in headspace volatile and CO_2 concentration, expressed as percentage, in (left) roasted coffee beans and (right) roasted ground coffee stored at 25 °C in air (Nicoli *et al.*, 1993)

IPR2023-00485
Nespresso USA, Inc. Ex. 1056
Page 13 of 34

6.1.2.2 Effect of temperature

The temperature dependence of CO_2 and volatile release from roasted coffee can be well described by the Arrhenius equation. An example of an Arrhenius plot, referring to volatile release from roasted coffee beans, is shown in Figure 6.4. The corresponding activation energy was 28.1 kJ/mol, which gives a temperature sensitivity, expressed in terms of Q_{10}, of around 1.5. It means that, in the experimental conditions adopted, for any 10 °C increase, the rate of volatile release increased 1.5-fold. This result agrees with data on the temperature dependence of diffusion coefficients for CO_2, recently reported by Labuza *et al.* (2001). Moreover, the Q_{10} of CO_2 diffusion coefficients calculated for ground coffee were shown to be approximately twice those of the beans.

The importance of the temperature variations due to day–night fluctuations and to transport is difficult to assess. It may be assumed that, because of temperature changes, competing degradation reactions occur at different times, so that the resulting deterioration is likely to occur faster than at constant temperature. Besides temperature, additional factors affecting staling reaction rates of coffee during storage are a_w and O_2 availability.

6.1.2.3 Effect of moisture

Water in roasted coffee may have different origins: despite the strong dehydration occurring during the first stage of the roasting process, new

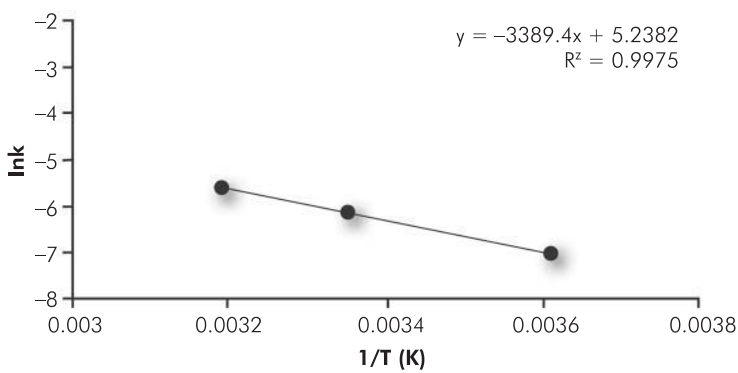

Figure 6.4 Arrhenius plot of volatile release from roasted coffee beans. Data are expressed as ln volatile release rate *vs.* temperature^{-1} (K). (Elaborated from Nicoli *et al.*, 1993)

IPR2023-00485
Nespresso USA, Inc. Ex. 1056
Page 14 of 34

water molecules are formed as a consequence of the Maillard reaction. Additional water may come by the use of water quenching instead of air-cooling. Furthermore, the eventual sorption of ambient moisture from roasted coffee during storage represents an additional cause of moisture and hence of a_w increase. Moisture sorption isotherms at 22 °C of roasted coffee beans and ground coffee are shown in Figure 6.5. Due to the higher exposed surface, which affects concentration and availability of polar active sites, ground coffee shows a considerable higher capacity to bind water molecules compared to beans.

In addition, depending on a_w, the bean structure can be brittle or elastic as shown in Figure 6.6.

It is well known that at normal storage temperatures the bean structure is brittle and easy to grind, as shown by the low fracture force measured for air-cooled roasted coffee samples with a_w values ranging at 0.1–0.2. This is due to the fact that roasted coffee beans are greatly below the glass transition temperature, which was recently observed to range from 130 to 170 °C (Karmas and Karel, 1994; Eggers and Pietsch, 2001). However, increasing a_w, the fracture force was shown to double up to a_w 0.85. This is due to the plasticizing effect of water responsible for a decrease in the glass transition temperature (*Tg*), making the coffee structure rubbery and more elastic. For a_w values higher than 0.85, solubilization of coffee compounds and a sharp decrease in the fracture force are detected.

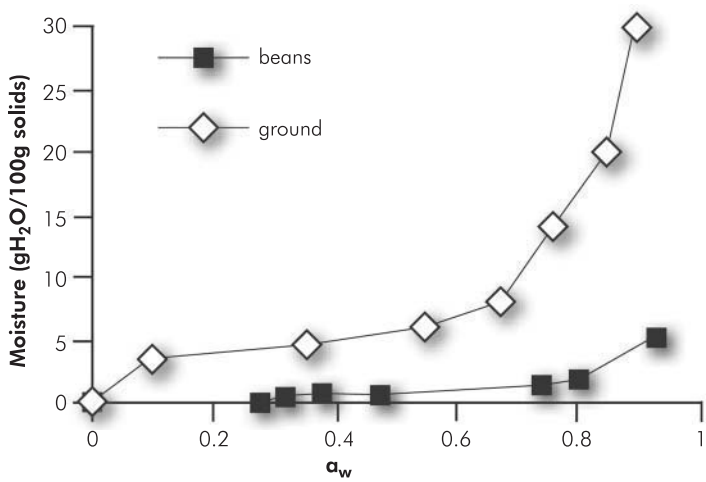

Figure 6.5 Moisture sorption isotherm at 22 °C of roasted coffee beans and ground coffee. (Data from Labuza *et al.*, 2001; Pittia, 2002)

IPR2023-00485
Nespresso USA, Inc. Ex. 1056
Page 15 of 34

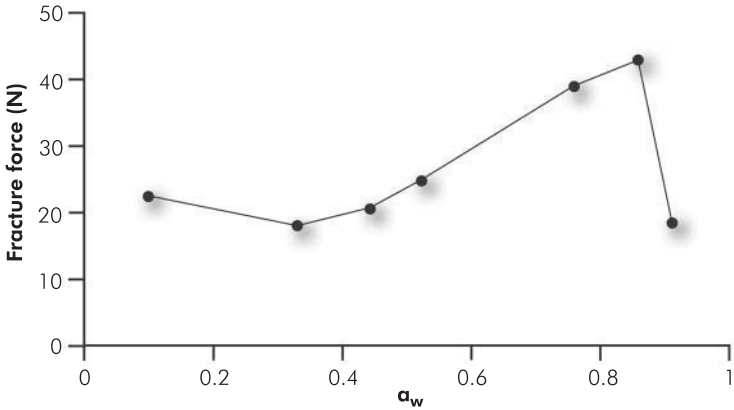

Figure 6.6 Changes in fracture force of dark roasted coffee beans as a function of water activity (Pittia, 2002)

6.1.2.4 Oxygen uptake

As mentioned above, oxidation reactions represent an additional cause of quality loss of roasted coffee during storage. In general terms the rate of all the oxidation reactions occurring in coffee, including those of aroma compounds, increases with increasing oxygen pressure, temperature and a_w. A study of the influence of these three variables on the overall oxidation rate of ground roasted coffee was recently reported by Cardelli and Labuza (2001). The oxygen uptake and sensorial evaluations were used as indicators of product acceptability. By matching the map of rate of food deterioration reactions as a function of water activity with the water sorption isotherm of roasted and ground coffee at room temperature it could be possible to understand what type of chemical reactions are involved in coffee deterioration. In coffee, moisture content ranges from 2% to 5%, which corresponds to 0.2–0.4 water activity. Using these data, it is evident that the oxidation of the coffee lipids is the prevalent reaction.

The influence of a_w and temperature on the shelf life of roasted ground coffee, calculated on the basis of the oxygen uptake index, is illustrated in Figure 6.7. On the basis of these results it can be stated that temperature has a smaller effect than moisture on the shelf life of the product.

The increase in the rate of degradation can be quantified, as a function of oxygen, by introducing a QO_2 index, which represents the relative variation of the rate of degradation caused by an increase in oxygen content of 1%. According to Cardelli and Labuza (2001), QO_2 is 10.5,

IPR2023-00485
Nespresso USA, Inc. Ex. 1056
Page 16 of 34

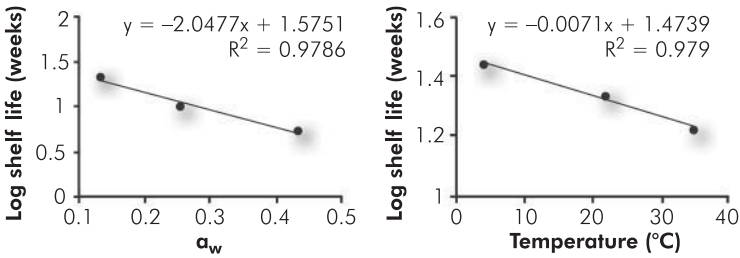

Figure 6.7 Water activity and temperature dependence of the shelf life of ground and roasted coffee (Labuza *et al.*, 2001)

when oxygen concentration is low (0.1–1.1%). It is 1.1 when oxygen increases up to 5%. Further increase of oxygen, up to 21%, does not affect the index, which remains 1.1. Summarizing, it can be stated that the rate of oxygen uptake increases 10-fold, from 0.1 to 1.1%; above 1.1% of oxygen concentration, for each 1% increase of oxygen there is a consequent increase for the rate of degradation of 10%.

6.1.3 Other physico-chemical changes

O. Savonitti

6.1.3.1 Volatile compounds

The aroma complex formed during roasting consists of several hundred compounds covering many different chemical classes. Some of them are stable and undergo no change during storage other than loss due to evaporation. Apparently, such compounds do not contribute much to the quality of the perceived aroma. Aroma-impact components are mainly unstable substances particularly prone to oxidation; some, aldehydes and ketones, are present in intermediate states of oxidation, whilst many more, alcohols, phenols, thiols, etc., are in a reduced form. There is then a significant risk of aroma changes occurring as a result of oxidation, particularly of compounds such as the thiols, which have very low threshold values.

The mechanisms responsible for the deterioration of aroma constituents have not yet been fully elucidated; immediately after roasting it may be simply due to evaporation and physical loss of the most volatile compounds; conversion to other volatile or non-volatile compounds, retained in the coffee matrix, also takes place; intermolecular reactions are also likely to occur – for instance, α-dicarbonyls and aldehydes can

IPR2023-00485
Nespresso USA, Inc. Ex. 1056
Page 17 of 34

bind to compounds containing free amino groups. These reactions are apparently influenced by the presence of atmospheric oxygen, suggesting an oxidative route to degradation. The change in aroma profile cannot be simply explained by the loss of the compounds affected, as the reaction products themselves may make a sensory contribution. In the case of thiols, for instance, the corresponding condensation products, the disulphides, have a major sensory impact, different from that of the fresh product. Afterwards, oxidation reactions become predominant, as indicated by the correlation between deterioration and oxygen uptake; and oxidation of the aroma complex will lead to a further dramatic shift in aroma quality.

Oxidation, responsible for the typical stale flavour of old coffee, is the sum of two actions: the loss of pleasant aroma components accompanied by the formation of off-flavours. A study has concentrated on identifying the compounds responsible for the freshness of coffee aroma, defined as the fine and pleasant smell arising from freshly roasted beans (Steinhart and Holscher, 1991). The conclusion was that low-boiling compounds – such as methanethiol, Strecker aldehydes and α-dicarbonyls – were the most important; in particular, loss of methanethiol was considered as the most important indicator. All of these compounds are volatile and extremely reactive species, therefore, easily oxidized. Figure 6.8 shows that their disappearance, particularly noticeable among those with the lowest boiling point, occurs mainly over the first three weeks of storage, and is principally due to evaporation.

Successive research during the 1990s led to a set of 28 compounds in roasted and ground coffee as the most odour-active components associated to fresh coffee aroma (Grosch, 1999, 2001; Czerny and Schieberle, 2001).

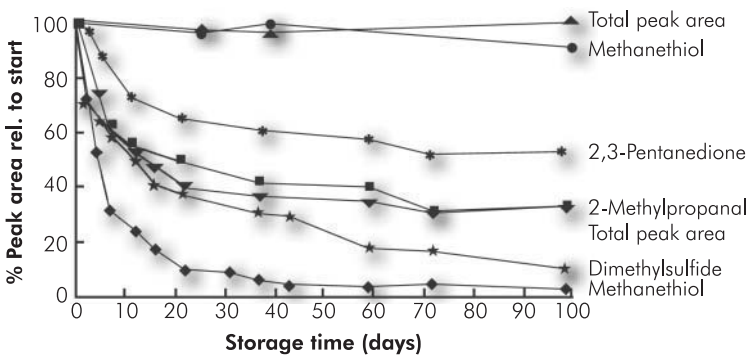

Figure 6.8 Loss of volatile compounds during storage

IPR2023-00485
Nespresso USA, Inc. Ex. 1056
Page 18 of 34

One of these, namely methanethiol, is frequently used in many freshness indices for coffee samples stored in different conditions (Sanz *et al.*, 2001). Many of these compounds can be used, in a definite linear combination, as indicators of the change of freshness for a roasted and ground coffee exposed to air at different temperatures (Cappuccio *et al.*, 2001).

The loss of volatile substances from coffee is not only related to their volatility, but also to the way they are trapped in the cells. In fact, two additional mechanisms of aroma retention play an important role. The cell wall consists of polar polysaccharides and melanoidins, which can adsorb and retain a wide range of volatile substances, particularly polar ones. Oil, on the contrary, preferentially retains lipophilic substances, such as alkylpyrazines, etc. In order to evaporate, volatile particles 'trapped' in the cell structure of the beans must first migrate across the cell walls. In ground coffee this is made easy by the small particle size, so that aroma loss occurs at a higher rate in ground coffee than in coffee beans and is inversely proportional to particle size. Hence, finely ground espresso blends lose their aroma just a few hours after being exposed to air, and start smelling stale due to oxidation, if not stored in packages. However, even in this case coffee aroma can undergo modifications through time, if stored in packages somehow permeable to oxygen. Coffee staling is associated with a degradation of some particular odorants, like odour-active aldehydes, α-dicarbonyls and thiols (2-furfurylthiol has the main impact), rather than to the creation of off-odorants. This is due again to the presence of oxygen, because of the non complete impermeability of the package (Czerny and Schieberle, 2001).

6.1.3.2 Non-volatile compounds

Production of carbon dioxide during roasting forms an effective barrier, which excludes most of the atmospheric oxygen from the cellular structure so delaying the onset of oxidation. As degassing goes on, lipid oxidation can no longer be stopped by the antioxidant activity of the Maillard reaction products formed during roasting (Homma, 2001; Steinhart *et al.*, 2001), and in a few months, at the end of degassing, the beans are rancid.

Ground coffee is particularly sensitive to oxidation because grinding removes the CO_2 barrier almost completely, while at the same time the oil–air contact surface dramatically increases, promoting oxygen uptake.

Lipids, an important fraction in roasted coffee, are easily oxidized during storage (Huynh-ba *et al.*, 2001). The major unsaturated fatty acid in coffee is linoleic acid ($C_{18:2}$), which contains two double bonds and is,

IPR2023-00485
Nespresso USA, Inc. Ex. 1056
Page 19 of 34

therefore, rather susceptible to oxidation. Figure 6.9 shows the reduction in linoleic acid content of rancid beans with respect to fresh beans; while the major saturated fatty acid, stearic acid ($C_{16:0}$), remains practically unchanged (Fourny *et al.*, 1982).

An important contribution to oxidation off-flavours is the formation of volatile aldehydes, such as *trans*-2-nonenal, the main breakdown product of lipid oxidation, which has an odour threshold level of 0.08 μg/l in water (Flament, 2002).

6.1.3.3 Oil migration

Oil migration starts during roasting and goes on during degassing because carbon dioxide tends to push oil outwards through the cell pores. The increase in oil viscosity at lower temperatures slows down the process.

Oil migration to the surface of the beans, where the risk of oxidation is maximal, is particularly important in fine ground dark espresso blends, since dark roasting leads both to fast degassing and to increased porosity, from disruption of cell walls. A further problem linked with oil exudation is the increase in stickiness of the particles, which tend to aggregate into lumps, making brewing irregular. The aggregation of particles on storage is worsened by the absorption of moisture, as discussed in 6.1.2.3.

6.1.3.4 Effect of light

Light plays a catalytic role in many chemical reactions; in the case of espresso (arabica) blends, particularly rich in unsaturated fatty acids, light

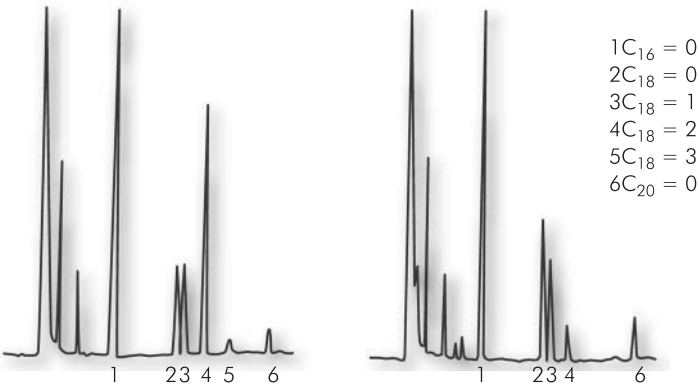

Figure 6.9 Fatty acid content of (left) fresh and (right) rancid beans

IPR2023-00485
Nespresso USA, Inc. Ex. 1056
Page 20 of 34

catalyses the prime trigger of their auto-oxidation reaction, i.e. the formation of $H^{\cdot}$, $R^{\cdot}$ (alkyl) and $ROO^{\cdot}$ (peroxide) free radicals which then cause the reaction to propagate.

6.2 PACKAGING OF ROASTED COFFEE

O. Savonitti

All the potential causes of deterioration highlight the importance of packaging. Indeed, it may be stated that, because of its instability, roasted coffee should either be consumed straight away or packaged in a water- and oxygen-tight container. Special packaging materials and techniques, with careful process monitoring, are required not to jeopardize the final quality by poor manufacturing practices.

6.2.1 Packaging materials

In order to meet total quality requirements (see Chapter 1) the package should:

- act as a barrier against water and moisture;
- act as a barrier against atmospheric oxygen;
- preserve coffee aroma and keep out foreign odours;
- be grease-proof;
- be light-proof;
- allow the carbon dioxide released during degassing to escape;
- be chemically inert;
- be hygienically safe and suitable for foodstuffs;
- be long-lasting;
- be sturdy and withstand pressure variations;
- be cheap;
- be practical;
- be environmentally friendly;
- be consumer-friendly.

Most of these requirements are aimed at preventing spoilage; some are exclusively intended to add value to consumers. Packaging materials should be grease-proof to prevent air oxidation of coffee oil leaking through the package, which would then spoil the beans. Chemical inertia of the material is also important, and metals or other substances, which could act as oxidation catalysts, should be avoided. Table 6.4 lists the materials meeting most of these packaging requirements.

IPR2023-00485
Nespresso USA, Inc. Ex. 1056
Page 21 of 34

Table 6.4 Materials commonly used for packaging roast coffee

Material	Advantages	Disadvantages
Tinplate	Total barrier Resistant to pressurse Satisfactory ecobalance* Recyclable Sturdy	Expensive Its rigidity prevents an optimal use of space
Aluminium	Total barrier Resistant to pressure Recyclable	Expensive Its rigidity prevents an optimal use of space Poor ecobalance Difficult to sort from other wastes
Glass	Total barrier Good ecobalance Recyclable Resistant to pressure	Fragility Heavy material Expensive Its rigidity prevents an optimal use of space Difficult to sort from other wastes
Combined flexible multi-ply polymer aluminium	Inexpensive Simple manufacturing technology Large flexibility and optimal use of space Satisfactory ecobalance	Non-tight barrier Resistant only to negative pressures Poor strength
Combined multi-ply aluminium cardboard	Inexpensive Total barrier Satisfactory ecobalance	Difficult to sort from other wastes Non resistant to pressure Poor strength Complex manufacturing technology
Flexible combined multi-ply polymer	Inexpensive Simple manufacturing technology Satisfactory CO_2 permeability No need to sort for other wastes	

*Ecobalance is defined as the total pollution resulting from energy consumption, and that resulting from the product, during manufacture, use and disposal.

Commonly used materials are the inexpensive flexible polymer-aluminium multi-ply, ensuring an efficient barrier and an optimal use of space all along the life cycle, and tinplate, particularly useful for positive pressure-resistant packages. The aluminium contained in multi-ply materials constitutes the only completely effective barrier; the inner layer is a film of waterproof weldable material; the centre layer is an

IPR2023-00485
Nespresso USA, Inc. Ex. 1056
Page 22 of 34

airtight aluminium film and the outer layer consists of a material that makes the structure more rigid and resistant to mechanical stress.

None of the materials listed in Table 6.4 ensures the level of permeability to carbon dioxide required to keep a stable internal pressure during degassing; other means must be applied.

Blow-moulded rigid plastic materials (HD-PE or PET) have lately been introduced for roast and ground coffee packaging: one-way valves on easy-peel-off membranes or applied directly on the packaging allow degassing and avoid deformations. This type of container is light, resistant to breakage, can be easily piled up, and recycled. Production technology is well known and the form can be chosen at will. However, the material does not provide a perfect barrier to gases.

6.2.2 Packaging techniques

The techniques used for packaging roast coffee are listed in order of increasing product protection:

- air packaging
- vacuum packaging
- inert gas packaging
- pressurization
- combined use of one of the previous techniques with active packaging.

6.2.2.1 Air packaging

Air packaging consists in simply filling and hermetically sealing the package; coffee is protected against humidity, off-flavours and light, but the presence of air inside the package means high oxygen levels and consequently shortened shelf life. This technique can only be used with degassed coffee to prevent swelling and possible explosion of the airtight package. If the coffee, particularly coffee beans, is not degassed, swelling can be prevented by fitting a one-way safety valve on the package allowing carbon dioxide to escape without letting air in. As CO_2 is heavier than air, it tends to stratify at the bottom expelling most of the oxygen gas; the flushing effect reduces residual oxygen and increases product shelf life. Air packaging using a one-way safety valve is an acceptable technique for air-cooled coffee beans since they contain large quantities of gas; its main disadvantage is that most of the aroma escapes together with CO_2, so dulling cup taste.

IPR2023-00485
Nespresso USA, Inc. Ex. 1056
Page 23 of 34

6.2.2.2 Vacuum packaging

Vacuum packaging meets two different objectives: air extraction with lowering of oxygen level, and use of flexible materials. The technique, which can also be used with rigid materials such as tinplate, is commonly applied to flexible materials to make the coffee 'bricks' sold in supermarkets. The box shape is obtained by an intimate contact between the material and the coffee, which must be completely degassed to avoid a decrease in compactness of the package provoked by a release of carbon dioxide making it floppy or swollen. This is why bricks are generally used only for packaging water-cooled ground coffee. Disadvantages of vacuum packaging in flexible containers are linked with water-cooling, which shortens product shelf life and may decrease yield. On the other hand, in rigid containers the internal vacuum widens the difference between the partial pressure of volatile aroma and ambient, so that more aroma volatilizes to saturate the headspace, dulling the cup. Furthermore, even if rigid containers can be strengthened by ribbing to prevent collapse, the vacuum level still remains less than in flexible bags.

6.2.2.3 Inert gas packaging

In inert gas packaging the air inside the container is replaced by inert gas either through the compensated vacuum technique or by flushing the inside of the package with inert gas. In the former case, first a vacuum is created in the package, then enough inert gas to balance the internal and external pressures is admitted. In the latter case, a drop of liquefied inert gas is placed on the bottom of the package, which evaporates pushing the air out. This process generally uses nitrogen or carbon dioxide which, although not an inert gas, behaves as such in a moisture-free environment and, moreover, is naturally present in roast coffee. The use of an inert gas for coffee packaging increases shelf life three-fold (see Table 6.5) with respect to vacuum packaging. Even with the same type of package – and therefore with the same permeability to oxygen and water vapour – the type of conditioning process will impact on the product's shelf life, and consequently on the cup (Alves *et al.*, 2001).

The pressure in the package is in equilibrium with the atmosphere at the moment of sealing. Just like in air packaging, to prevent internal pressure rising due to degassing, coffee must be either packed after degassing or the package fitted with a one-way valve.

From a legal standpoint the gas added to the package is considered a processing aid rather than an additive, since it dissipates on opening.

IPR2023-00485
Nespresso USA, Inc. Ex. 1056
Page 24 of 34

Table 6.5 Barrier properties of packaging materials for roasted coffee

Material	Permeability*	Barrier
Tinplate, glass aluminium		Complete
Three-ply with aluminium	<0.5	Very high
Three-ply with metal	0.5–3.0	High
Two-ply with metal	3.0–30	Moderate
Two-ply	30–150	Low
Single film, treated paper	>150	Very low

*Values expressed in:
cm^3/m^2 24 h bar at 23 °C and 0% R.H. for gases: gas volume (cm^3 of gas) that passes through 1 m^2 of surface in one day (24 hours), with one bar of pressure difference between the two layers at 23 °C and 0% of relative humidity g/cm^2 24 h bar at 38 °C and 90% R.H. for water values gas mass (grams of water vapour) that passes through 1 m^2 of surface in one day (24 hours), with one bar of pressure difference between the two layers at 38 °C and 90% of relative humidity.

6.2.2.4 Pressurization

Pressurization is the same as inert gas packaging except that the internal pressure is higher than atmospheric pressure. If coffee is immediately packaged after air-cooling, the pressure normally rises due to degassing. The packaging technique is the same as in compensated vacuum packaging, but in order to withstand pressure containers must be made of rigid materials, normally tinplate or aluminium; they must also be equipped with a safety valve opening when pressure increases by 0.5 atmospheres due to the large amount of gas released (see 6.1.2.1 and Figure 6.1).

Pressurization has an 'ageing' effect with quality improvement after 10–15 days. Indeed, an espresso cup prepared from an aged product has an improved body and aroma. The ageing may be explained by a binding of aroma constituents to the oil trapped within the cell structure. During degassing, pressure rises in the container and the reduced pressure gradient between the packaging environment and the bean structure produces two combined effects underlying the ageing mechanism: first, a decrease in degassing rate reduces oil migration so that more of it remains in the beans (Clarke, 1987b, p. 204); second, the pressure in the package becomes higher than the partial pressure of most volatile compounds

IPR2023-00485
Nespresso USA, Inc. Ex. 1056
Page 25 of 34

present in the cells, allowing for a larger quantity to be dissolved in the lipid phase or to bind to melanoidins.

Pressurization, by creating high pressure within the bean, also has the effect of spreading the oil on the cell walls to form an effective barrier against oxygen; this effect is clearly visible in Figure 6.10, which shows the cross-sections of, on the left, a non-pressurized roast bean, and, on the right, a pressurized one; caramelized material, containing lipids (dissolving volatile aroma), is shown in orange-yellow, while cell walls are reddish. (PIC IC B&W)

Due to the difference between internal bean pressure (which at the end of the degassing process reaches equilibrium with the pressure in the container) and atmospheric pressure, when the package is opened, there is still a residual amount of CO_2 in the beans to be released. Moreover, when oxygen enters the beans at the end of the degassing phase, oxidation is reduced because the aroma constituents are dissolved in the compacted lipid aggregates, so that, even once the package is open, a pressurized blend retains its fragrance longer than a blend packaged by other techniques.

6.2.2.5 Active packaging

The need to stress the performance of existing passive packages and related packaging techniques on one hand, and the need to guarantee an adequate product freshness on the other has brought the concept of 'active packaging' into consideration for coffee as well. Rooney (1995) defined active packaging as 'packaging that performs a role other than an inert barrier to the outside environment'. A more recent definition of active packaging is 'packaging that changes the condition of the packaged food to extend shelf life or improve food safety or sensory properties, while maintaining the quality of the packaged food'. This second definition has

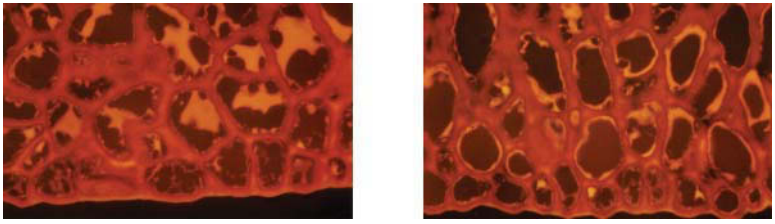

Figure 6.10 Cross-section of cells from (left) non-pressurized and (right) pressurized beans

IPR2023-00485
Nespresso USA, Inc. Ex. 1056
Page 26 of 34

been chosen for the European FAIR project Ct.98-4170. (De Kruijf *et al.*, 2002).

Active packaging systems can be classified into active scavenging systems (absorbers) and active-releasing systems (emitters). In the specific case of active coffee packaging, it includes oxygen and carbon dioxide scavengers. The oxygen scavenger has the precise task to eliminate residual oxygen present within the headspace of the packaging in the case of high barrier packages and conditioning in inert gas, or to eliminate the oxygen present, in the case of air packaging. In both cases, the elimination of oxygen contributes to extending the stability of the product during the storing phase. Moreover, independently from the conditioning used, in the case of permeable packaging, the oxygen absorber has the task of capturing oxygen entering through the walls of the package until it becomes saturated.

In general, the existing oxygen scavenger technologies are based on one or more of the following principles: (1) iron powder oxidation, (2) ascorbic acid oxidation, (3) photosensitive dye oxidation, (4) enzymatic oxidation, (5) unsaturated fatty acids and (6) yeast immobilized on solid material. They may be used as sachets inserted into the package, or be bonded by a label to the wall of the package. They can be used as linings in the closure of the package or can be dissolved, dispersed or immobilized in the polymer of the package material. The most commonly applied scavengers in coffee packaging are based on iron powder oxidation; their advantage is that they are in a position to reduce the level of oxygen below 0.01%, a value much lower than 0.3–3%, the residual values typically reached when applying a modified atmosphere packaging technique.

Carbon dioxide scavengers have the task of removing a proportion of the carbon dioxide released from the coffee in order to prevent the package from bursting when the coffee has not been previously degassed. They can represent an alternative use to the one-way valves or to materials permeable to carbon dioxide (which are in general also very permeable to oxygen and water vapour) (Vermeiren *et al.*, 1999).

A combined solution, such as dual action oxygen and carbon dioxide scavenger systems in the form of sachets or labels, is common in canned and foil-pouched coffees in Japan and the USA. This dual action system typically contains iron powder as oxygen scavenger and calcium hydroxide that scavenges carbon dioxide in the presence of high moisture levels (http://www.atalink.co.uk/pira/html/menu-packaging.htm 'A fresh approach', Brian Day Campden and Chorleywood Food Research Association). Some oxygen scavengers are subject to competition between oxygen and carbon dioxide; for this reason the dual action

IPR2023-00485
Nespresso USA, Inc. Ex. 1056
Page 27 of 34

system contains alkaline hydroxide specific for carbon dioxide (Matsushima *et al.*, 1995).

6.2.3 Control parameters

The packaging process starts from the selection of the packaging materials and techniques, through conditioning, when coffee is filled into the packs and sealed, to the final phase when bags and cans are stored and taken to the place of consumption. Each step of this long chain must be carefully monitored to prevent or at least correct all possible defects so that the quality (see 1.3) of the ready-to-use coffee blend complies with regulations and is up to consumers' expectations. Various parameters are monitored throughout the different phases of the packaging process.

6.2.3.1 Packaging material

The packaging material must be adapted to the packaging technique and to the intended shelf life. As mentioned in 6.2.1, the most important packaging requirements concern the barrier properties of the chosen material, i.e., its permeability to gas and moisture. Such barrier properties can be classified as shown above in Table 6.5.

Glass and metals are air- and watertight; the choice of packaging materials based on their barrier properties, therefore, only applies to multi-ply materials, which can be prepared from different polymers. Their permeability is a function of the type of polymer, of possible surface treatments on the polymer, their thickness and the combination chosen.

In addition to the packaging material, particularly in the case of tight containers, the packaging shape must also be decided. The main parameters to be considered in this choice are volume of headspace, which should be as small as possible to limit the amount of aroma volatilized to reach saturation equilibrium, and the ratio of volume to surface area, which should also be as low as possible, particularly when incomplete barrier materials are used, since permeability depends on surface area.

6.2.3.2 Choice of the packaging technique

As seen in 6.1.1, oxygen consumption is the main cause of deterioration of roast coffee, which should therefore be protected from entering into contact with oxygen as soon as roasted. The lower the level of residual

IPR2023-00485
Nespresso USA, Inc. Ex. 1056
Page 28 of 34

oxygen in the package, the longer the shelf life of the product. But the lower the amount of residual oxygen the more effective the package should be as a barrier to keep oxygen at the same level throughout the shelf life of the product. The best techniques to improve shelf life are, in decreasing order, pressurization, inert gas and vacuum packaging; the technique must be chosen as a function of the desired shelf life.

The choice of the most suitable material is also influenced by the degree to which it can withstand positive internal pressures, when coffee is pressurized, or negative ones, when it is vacuum packaged. Table 6.6 shows the implications of these two parameters on shelf life and packaging requirements.

6.2.3.3 Conditioning

When coffee is air-packed no conditioning is needed; packages are just filled up and sealed, the only parameter to be monitored being air tightness, as the package needs only to protect coffee from moisture pick-up.

In vacuum packaging, conditioning consists in creating a 300–500 mbar vacuum inside the pack before sealing it. The vacuum level must then be monitored, particularly in rigid cans, which might otherwise collapse. If the vacuum is replaced by inert gas, the applied gas pressure and/or the internal pressure of the package must be checked. Pressure levels near atmospheric pressure are normally applied, while valveless packages are conditioned under a slight vacuum.

In pressurization, conditioning consists in exactly the same process, but the cans are pressure-resistant and coffee is not degassed. In this case, in

Table 6.6 Packaging parameters

Technique	Residual O_2(%)	Shelf life (mth)	Absolute P_{int} (Atm)	Material
In air:				
tight	16–18	1	nRT/V	Rigid
with valve	10–12	3	1.01*	Indifferent
Under vacuum	4–6	4–6	0.3	Better flexible
Under inert atmosphere	1–2	6–8	1.01*	Indifferent
Under pressure	<1	>18	Up to 2.2	Rigid

*Pressure at which the valve opens.

addition to residual oxygen, the pressure in the package should also be monitored once degassing has made the package swell.

The airtight seal, already important in air packaging, becomes critical with all the other types of packages because any leak in the packaging material would allow oxygen in, drastically reducing shelf life.

Pressure is measured by standard pressure gauges; the airtight seal is checked by measuring residual oxygen and/or, in the case of positive internal pressures, by plunging the package in water and checking for leaks. Various sensor methods are available to measure residual oxygen levels.

6.2.3.4 Logistics

In logistics, pressure, temperature and time are the key parameters.

The pressure level must be monitored to avoid the risk of swelling or even explosion from a build-up of pressure in valveless packs. This is why air transportation of coffee should be avoided, unless pressurized compartments are available.

The spoilage rate of roasted coffee increases seven-fold with every 10 °C rise in temperature. Coffee should therefore be stored at low temperature. Furthermore, low temperatures slow down evaporation of volatile compounds, so that coffee kept at low temperature retains more aroma than at normal temperature, as recently confirmed on roasted and ground coffee in air by Cappuccio *et al.* (2001). Cooled coffee beans should, however, be left at room temperature for a few hours before grinding to trap the volatile aroma present in the cells in the oil and melanoidins; a large aroma loss at grinding might otherwise dull the flavour of the cup. In pressurized coffee the binding of aroma by oil is hindered if the oil becomes too viscous, as is the case at temperatures approaching 0 °C; pressurized coffee should therefore be kept at room temperature for a few days after packaging. Temperature fluctuations should be avoided as they accelerate spoilage.

The last parameter to be monitored is time, i.e. the total storage period, which should always be kept shorter than the actual shelf life of the product. On average, coffee is consumed within three months from production which makes time a critical factor only for the least sophisticated packaging techniques.

6.2.3.5 Testing of finished products

Although lipid oxidation plays a major role in coffee deterioration, the peroxide test, commonly performed to assess rancidity in foods, is not

IPR2023-00485
Nespresso USA, Inc. Ex. 1056
Page 30 of 34

sensitive enough for coffee. Peroxides reach significant levels only in the very last stages of spoilage, when coffee has already become undrinkable.

Linoleic acid content is another parameter of little use to analysts, as it requires reference values measured on the same blend when fresh.

Electron spin resonance (ESR) measurements have also been carried out to detect the presence of free radicals; the intensity of the ESR signal has been found to be inversely related to the level of perceived acidity, which rises with deterioration; however, even this technique is not sensitive enough.

The concentration of specific volatile compounds in the headspace of the package or of the cup, measured by gas chromatography, has been used to determine the degree of spoilage. For instance, the ratio of 2-methylfuran to butanone, the 'aroma index' M/B, drops from 3.2 in fresh coffee to 2.3 in spoilt coffee. However, such indices depend on blend composition and on roasting technique, normally unknown to the analyst, so that these parameters can only be relied on to a very limited extent.

None of the test methods available can yet replace sensory evaluation, and tasting remains the most reliable of all test methods.

References

Alves R.M.V., Mori E.E., Milanez C.R. and Padula M. (2001) Roasted and ground coffee in nitrogen gas flushing packages. *Proc. 19th ASIC Coll.*, CD-ROM.

Anese M. and Nicoli M.C. (2003) Antioxidant properties of ready-to-drink coffee brews. *J. Agric. Food Chem.* 51, 942–946.

Anese M., De Pilli T., Massini R. and Lerici C.R. (2000) Oxidative stability of the lipid fraction in roasted coffee. *Ital. J. Food Sci.* 12, 457–463.

Anese M., Manzocco L. and Maltini E. (2001) Determination of the glass transition temperatures of solution 'A' and HMW melanoidins and estimation of viscosities by WLF equation: a preliminary study. In J. Ames (ed.), *Melanoidins in Food and Health Volume 2*, Proceedings of COST Action 919 workshop held at the Technical University of Berlin, 7–8 April 2000 and the Institute of Chemical Technology, Prague 22–23 September 2000, pp. 137–141; EUR 19684 EN, Belgium.

Barbera C.E. (1967) Gas-volumetric method for the determination of the internal non odorous atmosphere of coffee beans. *Proc. 3rd ASIC Coll.*, pp. 436–442.

Cappuccio R., Full G., Lonzaric V. and Savonitti O. (2001) Staling of roasted and ground cofffee at different temperatures: combining sensory and GC analysis. *Proc. 19th ASIC Coll.*, CD-ROM.

Cardelli C. and Labuza T.P. (2001) Application of Weibull hazard analysis to the determination of the shelf life of roasted and ground coffee. *Lebensm. Wiss. Technol.* 34, 273–278.

IPR2023-00485
Nespresso USA, Inc. Ex. 1056
Page 31 of 34

Clarke R.J. (1987a) Packing of roast and instant coffee. In R.J. Clarke and R. Macrae (eds), *Coffee: Volume 2 – Technology*. London: Elsevier Applied Science, pp. 201–215.

Clarke R.J. (1987b) Roasting and grinding. In R.J. Clarke and R. Macrae (eds), *Coffee: Volume 2 – Technology*. London: Elsevier Applied Science, pp. 73–197.

Clarke R.J. and Macrae R. (eds) *Coffee: Volume 2 – Technology*. London: Elsevier Applied Science.

Czerny M. and Schieberle P. (2001) Changes in roasted coffee aroma during storage – influence of the packaging. *Proc. 19th ASIC Coll.*, CD-ROM.

Daglia M., Papetti A., Gregotti C., Bertè F. and Gazzani G. (2000) In vitro antioxidant and ex vivo protective activities of green and roasted coffee. *J. Agric. Food Chem.* 48, 1449–1454.

De Krujf N., Van Beest M., Rijk R. J., Sipilainen-Malm T., Paseiro Losada P. and De Meulenaer B. (2002) Active and intelligent packaging: applications and regulatory aspects. *Food Addit. Contam.* 19, 144–162.

Eggers R. and Pietsch A. (2001) Technology I: Roasting. In R.J. Clarke and O.G. Vitzhum (ed.), *Coffee: Recent Developments*. Oxford: Blackwell Science, pp. 90–107.

Einarson H. (1987) The effect of time, temperature, pH and reactants on the formation of antibacterial compounds in the Maillard reaction. *Lebensm. Wiss. Technol.* 20, 51–55.

Faist V. and Erbesdobler H.F. (1999) In vivo effects of melanoidins. In J. Ames (ed.), *Melanoidins in Food and Health Volume 1*. Proceedings of COST Action 919. Workshop held at the University of Reading, UK, 2–4 December 1999, pp. 79–88; EUR 19684 EN Belgium.

Flament I. (2002) *Coffee Flavor Chemistry*. New York: Wiley & Sons, p. 118.

Fourny G., Cross E. and Vincent J.C. (1982) Etude préliminaire de l'oxidation de l'huile de café. *Proc. 10th ASIC Coll.*, pp. 235–246.

Full G., Savonitti O. and Cappuccio R. (2001) Staling of roasted and ground coffee at different temperatures: combining sensory and GC analysis. *Proc. 19th ASIC Coll.*, CD-ROM.

Goodman B.A., Pascual E.C. and Yeretzian C. (2001) Free radicals and other paramagnetic ions in soluble coffee. *Proc. 19th ASIC Coll.*, CD-ROM.

Grosch W. (1999) Key odorants of roasted coffee: evaluation, release, formation. *Proc. 18th ASIC Coll.*, pp. 17–26.

Grosch W. (2001) Chemistry III. Volatile compounds. In R.J. Clarke and O.G. Vitzthum (eds), *Coffee: Recent Developments*. Oxford: Blackwell Science, pp. 68–90.

Hodge J.E. (1953) Chemistry of browning reaction in model systems. *J. Agric. Food Chem.* 1, 928–943.

Hofmann T. (2000) Isolation, separation and structure determination of melanoidins. In J. Ames (ed.), *Melanoidins in Food and Health – Volume 1*, Proceedings of COST Action 919, Workshop held at the University of Reading, UK, 2–4 December 1999, pp. 31–43; EUR 19684 EN.

Hofmann T., Czerny M., Calligaris S. and Schieberle P. (2001) Model studies on the influence of coffee melanoidins on flavour volatiles of coffee beverages. *J. Agric. Food Chem.* 49, 2382–2386.

Homma S. (2001) In R.J. Clarke and O.G. Vitzthum (eds), *Coffee: Recent Developments*. Oxford: Blackwell Science, pp. 50–68.

Homma S., Aida K. and Fujumaki M. (1986) Chelation of metals with brown pigments in coffee. In M. Fujimaki, H. Kato and M. Namiki (eds), Amino-Carbonyl Reactions in Food and Biological Systems. Amsterdam: Elsevier, pp. 165–172.

Huynh-Ba T., Courtet-Compondu M.C., Fumeaux R. and Pollien Ph. (2001) Early lipid oxidation in roasted and ground coffee. *Proc. 19th ASIC Coll.*, CD-ROM.

Karmas R. and Karel M. (1994) The effect of glass transition on Maillard browning in food models. In T.P. Labuza, G.A. Reineccius, V. Monnier, J. O'Brien and J. Baynes (eds), *Maillard Reaction in Chemistry, Food and Health*. Cambridge: The Royal Society of Chemistry, pp. 164–169.

Labuza T.P., Cardelli C., Andersen B. and Shimoni E. (2001) Physical chemistry of carbon dioxide equilibrium and diffusion in tempering and effect on shelf life of fresh roasted ground coffee. *Proc. 19th ASIC Coll.*, CD-ROM.

Manzocco L., Calligaris S., Mastrocola D., Nicoli M.C. and Lerici C.R. (2001) Review of non-enzymatic browning and antioxidant capacity of processed foods. *Trends Food Sci. Technol.* 11, 340–346.

Manzocco L., Calligaris S. and Nicoli M.C. (2002) Assessment of pro-oxidant activity of foods by kinetic analysis of crocin bleaching. *J. Agric. Food Chem.* 50, 10.

Massini R., Nicoli M.C., Cassarà A. and Lerici C.R. (1990) Study on physico- and physico-chemical changes in coffee beans during storage. Note 1. *Ital. J. Food Sci*, 2, 123–130.

Matsushima T., Oguro N. and Ichiyanagi S. (1995) Stability improvement of roasted and ground coffee by oxygen absorbent. *Proc. 16th ASIC Coll.*, pp. 426–434.

Namiki M. (1990) Antioxidants/antimutagens in food. *Crit. Rev. Food Sci. Nutr.* 29, 273–300.

Nicoli M.C., Anese M., Manzocco L. and Lerici C.R. (1997) Antioxidant properties of coffee brews in relation to the roasting coffee. *Lebensm. Wiss Technol.* 30, 292–297.

Nicoli M.C., Anese M. and Calligaris S. (2001) Antioxidant properties of ready-to drink coffee beverages. *Proc. 19th ASIC Coll.*, CD-ROM.

Nicoli M.C., Innocente N., Pittia P. and Lerici C.R. (1993) Staling of roasted coffee: volatile release and oxidation reactions during storage. *Proc. 15th ASIC Coll.*, pp. 557–566.

Nicoli M.C., Toniolo R. Anese M. (2004) Relationship between redox potential and chain-breaking activity of model systems and foods. *Food Chem.* 88, 79–83.

O'Brian J. and Morissey P.A. (1989) Nutritional and toxicological aspects of Maillard browning reaction in food. *Crit. Rev. Food Sci. Nutr.* 28 (3), 221–248.

Pittia P. (2002) Personal communication.

Radtke R. (1979) Zur kenntnis des sauerstoffverbrauchs von rostkaffee und seiner auswirkung auf die sensoriesch ermitelte qualitata des kaffeegetranks. *Chem. Mikrobiol. Technol. Lebensm.* 6, 36–42.

Rooney M.L. (1995) Overview of active food packaging. In M.L. Rooney (ed.), *Active Food Packaging*. New York: Blackie Academic and Professional/Chapman and Hall, pp. 1–37.

Sanz C., Pascual L., Zapelena M.J. and Cid M.C. (2001) A new 'aroma Index' to determine the aroma quality of a blend of roasted coffee beans. *Proc. 19th ASIC Coll.*, CD-ROM.

Sheikh-Zeinoddin M., Perehinec T.M., Hill S.E. and Rees C.E.D. (2000) Maillard reaction causes suppression of virulence gene expression in *Listeria monocytogenes*. *Int. J. Food Micr.* 61 (1), 41–49.

Shimoni E. and Labuza T.P. (2000) Degassing kinetics and sorption equilibrium of carbon dioxide in fresh roasted and ground coffee. *J. Food Process Eng.* 23, 419–436.

Sivetz M. and Desrosier N. (1972) *Coffee Technology*. Westport, CT: AVI Publishing.

Steinhardt H. and Holscher W. (1991) Storage related changes of low-boiling volatiles in whole beans. *Proc. 14th ASIC Coll.*, pp. 156–174.

Steinhart G., Luger A. and Piost J. (2001) Antioxidative effect of coffee melanoidins. *Proc. 19th ASIC Coll.*, CD-ROM.

Vermeiren L., Devlieghere F., Van Beest M., de Krujf N. and Debevere J. (1999) Developments in the active packaging of foods. *Trends in Food Sci. Technol.* 10, 77–86.

Whitfield F.B. (1992) Volatiles from interactions of Maillard reactions and lipids. *Crit. Rev. Food Sci. Nutr.* 31(1/2), 1–58.

Yaylayan V.A. and Huyghues-Despointes A. (1994) Chemistry of Amadori rearrangement products: analysis, synthesis, kinetics, reactions and spectroscopic properties. *Crit. Rev. Food Sci. Nutr.* 34 (4), 321–369.